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(54) Title: BREATHABLE LAMINATE OF NONWOVEN AND ELASTOMERIC FILM INCLUDING METALLOCENE CATALYZED POLYETHYLENE ELASTOMER AND METHOD FOR MAKING THE SAME		
(57) Abstract <p>The present invention relates to a breathable laminate including a breathable film and a support layer. The film includes a metallocene derived polyethylene elastomeric material and filler that contributes to pore formation. The present invention is also directed to a method of making the breathable laminate that includes stretching the film to form micropores therein, and bonding the film to the support layer.</p>		

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- 1 -

**BREATHABLE LAMINATE OF NONWOVEN AND ELASTOMERIC FILM
INCLUDING
METALLOCENE CATALYZED POLYETHYLENE ELASTOMER
AND METHOD FOR MAKING THE SAME**

FIELD OF INVENTION

The present invention is directed to breathable elastomeric films utilizing metallocene catalyzed polyethylene elastomers. In addition, the present invention is directed to a method of making such films. The invention also includes breathable laminates of the films to one or more substrates, and methods of making the laminates.

BACKGROUND OF THE INVENTION

The present invention is directed to breathable elastomeric films. Such materials have a wide variety of uses, especially in the areas of limited use and disposable items.

Films have been traditionally used to provide barrier properties in limited use or disposable items. By limited use or disposable, it is meant that the product and/or component is used only a small number of times or possibly only once before being discarded. Examples of such products include, but are not limited to, surgical and health care related products such as surgical drapes and gowns, disposable work wear such as coveralls and lab coats and personal care absorbent products such as diapers, training pants, incontinence garments, sanitary napkins, bandages, wipes and the like. In personal care absorbent products such as infant diapers and adult incontinence products, films are used as the outer covers with the purpose of preventing body wastes from contaminating the clothing, bedding and other aspects of the surrounding environment of use. In the area of protective apparel including hospital gowns,

- 2 -

films are used to prevent cross exchange of microorganisms between the wearer and the patient.

While these films can be effective barriers, they are not aesthetically pleasing because their surfaces are smooth and either feel slick or tacky. They are also visually flat and "plasticity" thereby making them less desirable in apparel applications and other uses where they are in contact with human skin. It would be more preferable if these items were more cloth-like from both a tactile and visual standpoint. For example, infant diapers that have the feel and appearance of traditional cloth undergarments are perceived as premium products and may, in some cases, overcome the tendency to believe that they need to be covered by outer garments for aesthetic reasons. Garment-like adult incontinence products could improve the self-image of the incontinent individual. In addition, more garment-like isolation gowns would help the hospital environment feel less foreign and threatening to the patient and increase the comfort of the wearer. It is also preferable to have films that can make an outercover material with more elastic give and recovery to provide better fit and comfort.

Lamination of films have been used to create materials which are both impervious and somewhat cloth-like in appearance and texture. The outer covers on disposable diapers are but one example. In this regard, reference may be had to coassigned U.S. Patent No. 4,818,600 dated April 4, 1989 and U.S. Patent No. 4,725,473 dated February 16, 1988. Surgical gowns and drapes are other examples. See, in this regard, coassigned U.S. Patent No. 4,379,102 dated April 5, 1983.

A primary purpose of the film in such laminations is to provide barrier properties. There is also a need for such laminates to be breathable so that they have the ability to transmit moisture vapor. Apparel made from laminations of these breathable or microporous films are

- 3 -

more comfortable to wear by reducing the moisture vapor concentration and the consequent skin hydration underneath the apparel item.

There is therefore a need for an elastic breathable film and process that provides a film with both the cloth-like aesthetics and the fit and comfort that are desired.

SUMMARY OF THE INVENTION

The present invention relates to a breathable elastomeric film that includes a metallocene catalyzed polyethylene polymeric resin material and at least 30% by weight of a filler having a particle size that contributes to pore formation. Preferably, the polymeric resin material has a density of from about 0.850 to about 0.917 g/cc. Preferably, the film includes from about 45 to about 60% filler by weight of the filled resin .

In one embodiment of the present invention, the resin material is selected from copolymers of ethylene and 1-butene, copolymers of ethylene and 1-hexene, copolymers of ethylene and 1-octene and combinations thereof. For certain applications of the present invention, the breathable film has an immediate recovery length that is at least about 50% of its elongation following a stretch cycling that achieved a stretched length of about 160% of the unbiased length. In yet other applications, the film of the present invention may have an immediate recovery length that is at least about 50% its elongation length following a stretch cycling that achieved a stretched length of about 200% of the unbiased length.

The present invention also is directed to a process for preparing a breathable elastomeric film of the present invention, including providing a polymeric resin including a metallocene catalyzed polyethylene polymeric material; adding to the polymeric resin at least 30% by

- 4 -

weight of a filler having a particle size that contributes to pore formation to form a filled resin; forming a film having a first length from the filled resin; and stretching the film to form a microporous film. The process of the invention is applicable to films formed by various processes, i.e., cast or blown films. In one embodiment of the invention, the microporous film is stretched to a second length that is from about 160 to about 400% of the first length.

The preferred film of the present invention has a water vapor transmission rate (WVTR) of from about 300 to about 4,500 grams per square meter per 24 hours (measured by ASTM Test E 96-80 with Celgard® 2500 as control). More preferably, the film of the present invention has a WVTR of from about 1,000 to about 4,000 g/m² 24 hrs.

Such films have a wide variety of uses including, but not limited to, applications in personal care absorbent articles including diapers, training pants, sanitary napkins, incontinence devices, bandages and the like. These same films also may be used in items such as surgical drapes and gowns as well as various articles of clothing either as the entire article or simply as a component thereof.

Having thus described the invention in detail, it should be appreciated that various modifications and changes can be made to the present invention without departing from the spirit and scope of the following claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic side view of a process for forming a laminate according to the present invention.

Figure 2 is a cross-section side view of a film/nonwoven laminate according to the present invention.

- 5 -

Figure 3 is a partially cut away top plan view of an exemplary personal care absorbent article, in this case a diaper, which may utilize a film made according to the present invention.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to breathable elastomeric films that include metallocene-catalyzed ethylene-based polymers.

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The term "metallocene-catalyzed ethylene-based polymers" as used herein includes those polymer materials that are produced by the polymerization of at least ethylene using metallocenes or constrained geometry catalysts, a class of organometallic complexes, as catalysts. For example, a common metallocene is ferrocene, a complex with a metal sandwiched between two cyclopentadienyl (Cp) ligands. Metallocene process catalysts include bis(n-butylcyclopentadienyl)titanium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)scandium chloride, bis(indenyl)zirconium dichloride, bis(methylcyclopentadienyl)titanium dichloride, bis(methylcyclopentadienyl)zirconium dichloride, cobaltocene, cyclopentadienyltitanium trichloride, ferrocene, hafnocene dichloride, isopropyl(cyclopentadienyl,-1-flourenyl)zirconium dichloride, molybdocene dichloride, nickelocene, niobocene dichloride, ruthenocene, titanocene dichloride, zirconocene chloride hydride, zirconocene dichloride, among others. A more exhaustive list of such compounds is included in U.S. Patent No. 5,374,696 to Rosen et al. and assigned to the Dow Chemical Company. Such compounds are also discussed in U.S. Patent No. 5,064,802 to Stevens et al. and also assigned to Dow.

The metallocene process, and particularly the catalysts and catalyst support systems are the subject of

- 6 -

a number of patents. U.S. Patent No. 4,542,199 to Kaminsky et al. describes a procedure wherein MAO is added to toluene, the metallocene catalyst of the general formula (cyclopentadienyl)₂MeRHal wherein Me is a transition metal, Hal is a halogen and R is cyclopentadienyl or a C1 to C6 alkyl radical or a halogen, is added, and ethylene is then added to form polyethylene. U.S. Patent No. 5,189,192 to LaPointe et al. and assigned to Dow Chemical describes a process for preparing addition polymerization catalysts via metal center oxidation. U.S. Patent No. 5,352,749 to Exxon Chemical Patents, Inc. describes a method for polymerizing monomers in fluidized beds. U.S. Patent No. 5,349,100 describes chiral metallocene compounds and preparation thereof by creation of a chiral center by enantioselective hydride transfer.

Co-catalysts are materials such as methylaluminoxane (MAO) which is the most common, other alkylaluminums and boron containing compounds like tris(pentafluorophenyl)boron, lithium tetrakis(pentafluorophenyl)boron, and dimethylanilinium tetrakis(pentafluorophenyl)boron. Research is continuing on other co-catalyst systems or the possibility of minimizing or even eliminating the alkylaluminums because of handling and product contamination issues. The important point is that the metallocene catalyst be activated or ionized to a cationic form for reaction with the monomer(s) to be polymerized.

The metallocene-catalyzed ethylene-based polymers used in the present invention impart stretch and recovery properties to the film. Preferably, the metallocene catalyzed ethylene-based polymer is selected from copolymers of ethylene and 1-butene, copolymers of ethylene and 1-hexene, copolymers of ethylene and 1-octene and combinations thereof. In particular, preferred materials include Affinity™ brand elastomeric

- 7 -

metallocene-derived copolymers of ethylene and 1-octene, both available from Dow Plastics of Freeport, Texas. Particularly preferred materials also include Exact™ brand elastomer metallocene-derived copolymers and terpolymers of ethylene and 1-butene and copolymers of ethylene and 1-hexene, available from Exxon Chemical Company of Houston, TX.

Useful metallocene catalyzed polyethylene elastomers are available in a variety of densities. Preferably, the material used in the present invention has a density of from about 0.850 to about 0.899 g/cc. More preferably, the material used in the present invention has a density of from about 0.860 to about 0.899 g/cc, even more preferably from about 0.870 to about 0.899 g/cc. The melt index range of some useful materials is between about 1 to about 15 dg/min and advantageously may be in the range of from about 5 to about 10 dg/min. Specific examples of suitable materials can be found in U.S. Patent Nos. 5,472,775 and 5,272,236, both assigned to the Dow Chemical Company. The entire content of these patents is incorporated herein by reference.

In addition to the polymeric material, the film layer also includes a filler which enables development of micropores during orientation of the film. As used herein, a "filler" is meant to include particulates and other forms of materials which can be added to the polymer and which will not chemically interfere with or adversely affect the extruded film but is able to be uniformly dispersed throughout the film. Generally, the fillers will be in particulate form and usually will have somewhat of a spherical shape with average particle sizes in the range of about 0.5 to about 8 microns. In addition, the film will usually contain at least 30 percent(%), preferably about 40 to about 70 percent, filler based upon the total weight of the film layer. More preferably, from about 45 to about 60 percent of

- 8 -

filler is present in the film. Both organic and inorganic fillers are contemplated to be within the scope of the present invention provided that they do not interfere with the film formation process, the breathability of the resultant film or its ability to bond to another layer such as a fibrous polyolefin nonwoven web.

Examples of fillers include calcium carbonate (CaCO_3), various kinds of clay, silica (SiO_2), alumina, barium sulfate, sodium carbonate, talc, magnesium sulfate, titanium dioxide, zeolites, aluminum sulfate, cellulose-type powders, diatomaceous earth, magnesium sulfate, magnesium carbonate, barium carbonate, kaolin, mica, carbon, calcium oxide, magnesium oxide, aluminum hydroxide, pulp powder, wood powder, cellulose derivative, polymer particles, chitin and chitin derivatives. The filler particles may optionally be coated with a fatty acid, such as stearic acid, and behenic acid which may facilitate the free flow of the particles (in bulk) and their ease of dispersion into the polymer matrix.

Generally, it has been possible to produce films with a water vapor transmission rate (WVTR) of at least about 300 grams per square meter per 24 hours, measured by the ASTM E-96-80 WVTR test. In general, factors that affect the amount of breathability include the amount of filler, the film stretching conditions (e.g., whether it is performed at ambient or elevated temperatures), orientation ratio, and film thickness. Preferably, the WVTR of the film of the present invention that may be used as a component in a limited-use or disposable item is from about 300 to about 4,500, more preferably from about 1,000 to about 4,000 $\text{g/m}^2/24$ hrs. In addition, the preferred films of the present invention are also elastic.

- 9 -

The term "elastic" is used herein to mean any material which, upon application of a biasing force, is stretchable, that is, elongatable, to a stretched, biased length which is at least about 150 percent of its relaxed unbiased length, and which will recover at least 50 percent of its elongation upon release of the stretching, elongating force. A hypothetical example would be a one (1) inch sample of a material which is elongatable to at least 1.50 inches and which, upon being elongated to 1.50 inches and released, will recover to a length of not more than 1.25 inches. Many elastic materials may be stretched by much more than 50 percent of their relaxed length, for example, 100 percent or more, and many of these will recover to substantially their original relaxed length, for example, to within 105 percent of their original relaxed length, upon release of the stretching force.

As used herein, the term "nonelastic" refers to any material which does not fall within the definition of "elastic," above.

These properties can be obtained by first preparing a polymeric resin of a metallocene catalyzed ethylene-based polymer filling the resin with filler, extruding a film from the filled resin and thereafter stretching or orienting the filled film in at least one direction, usually, the machine direction. As explained in greater detail below, the resultant film is microporous and has increased strength properties in the orientation direction.

Processes for forming filled films and orienting them are well-known to those skilled in the art. Figure 1 illustrates a general approach in orienting a filled film 10, such as one of the present invention. Referring to Figure 1, filled film 10 is unwound and directed to a film stretching unit 44 such as a machine direction orienter, which is a commercially available device from

- 10 -

vendors such as the Marshall and Williams Company of Providence, Rhode Island. Such an apparatus 44 has a plurality of stretching rollers 46 moving at progressively faster speeds relative to the pair disposed before it. These rollers 46 apply an amount stress and thereby progressively stretch filled film 10 to a stretch length in the machine direction of the film which is the direction of travel of filled film 10 through the process as shown in Figure 1. The stretch rollers 46 may be heated for better processing. Preferably, unit 44 also include rollers (not shown) upstream and/or downstream from the stretch rollers 46 that can be used to preheat the film 10 before orienting and/or anneal (or cool) it after stretching.

At the stretched length, a plurality of micropores form in the film 10. Preferably, the stretched length is from about 160 to about 500%, more preferably from about 200 to about 400% of the unbiased length of the film prior to stretching. If desired, film 10 is directed out of apparatus 44 so that the stress is removed to allow the stretched film 10 to relax.

Oftentimes it may be desirable to laminate filled film 10 to one or more substrates or support layers 20 such as is shown in Figure 2. Lamination of film may enhance the strength and thus durability of the film. If desired, filled film 10 may be attached to one or more support layers 30 to form a laminate 32. Referring again to Figure 1, a conventional fibrous nonwoven web forming apparatus 48, such as a pair of spunbond machines, is used to form the support layer 30. The long, essentially continuous fibers 50 are deposited onto a forming wire 52 as an unbonded web 54 and the unbonded web 54 is then sent through a pair of bonding rolls 56 to bond the fibers together and increase the tear strength of the resultant web support layer 30. One or both of the rolls are often heated to aid in bonding. Typically, one of

- 11 -

the rolls 56 is also patterned so as to impart a discrete bond pattern with a prescribed bond surface area to the web 30. The other roll is usually a smooth anvil roll but this roll also may be patterned if so desired. Once filled film 10 has been sufficiently stretched and the support layer 30 has been formed, the two layers are brought together and laminated to one another using a pair of laminating rolls or other means 58. As with the bonding rolls 56, the laminating rolls 58 may be heated. Also, at least one of the rolls may be patterned to create a discrete bond pattern with a prescribed bond surface area for the resultant laminate 32. Generally, the maximum bond point surface area for a given area of surface on one side of the laminate 32 will not exceed about 50 percent of the total surface area. There are a number of discrete bond patterns which may be used. See, for example, Brock et al., U.S. Patent No. 4,041,203 which is incorporated herein by reference in its entirety. Once the laminate 32 exists the laminating rolls 58, it may be wound up into a roll 60 for subsequent processing. Alternatively, the laminate 32 may continue in-line for further processing or conversion.

While the support layers 30 and film 10 shown in Figure 1 were bonded together through thermal point bonding, other bonding means can also be used. Suitable alternatives include, for example, adhesive bonding and the use of tackifiers. In adhesive bonding, an adhesive such as a hot melt adhesive is applied between the film and fiber to bind the film and fiber together. The adhesive can be applied by, for example, melt spraying, printing or meltblowing. Various types of adhesives are available, including those produced from amorphous polyalphaolefins, ethylene vinyl acetate-based hot melts, and Kraton® brand adhesives available from Shell Chemical

- 12 -

of Houston, TX and Rextac™ Brand Adhesives from Rexene of Odessa, TX.

When the film and support layer(s) is bonded with tackifiers, the tackifier may be incorporated into the film itself. The tackifier essentially serves to increase adhesion between the film and fiber layers. The film and fiber laminate may subsequently be thermally point-bonded, although generally very little heat is required since the tackifier tends to increase the pressure sensitivity of the film and a bond somewhat like and adhesive bond can be formed. Examples of useful tackifiers include Wingtack™ 95, available from Goodyear Tire & Rubber Co. of Akron, OH, and Escorez™ 5300, available from Exxon Chemical Company of Houston, TX.

The direction of elasticity in the laminate may be tailored by the state of the film, i.e., whether it is relaxed or stretched, during the bonding with the support layer, as well as the physical property of the support layer material. For example, if the film is relaxed prior to bonding and the support layer is extensible in the cross-machine direction ("CD"), then a laminate with both CD and machine-direction ("MD") stretch can be produced. Additionally, if the film is bonded to a support layer non-extensible in the CD direction while in a stretched state, then a laminate with a MD stretch can be produced.

The support layers 30 as shown in Figure 2 are fibrous nonwoven webs. The manufacture of such fibrous nonwoven webs is known. Such fibrous nonwoven webs can add additional properties to filled film 10, such as a more soft, cloth-like feel. This is particularly advantageous when filled film 10 is being used as a barrier layer to liquids in such applications as outer covers for personal care absorbent articles and as barrier materials for hospital, surgical, and clean room applications such as, for example, surgical drapes, gowns

- 13 -

and other forms of apparel. Attachment of the support layers 30 to the filled film 10 may be by the use of a separate adhesive such as hot-melt and solvent based adhesives or through the use of heat and/or pressure (also known as thermal bonding) as with heated bonding rolls.

The support layer in a laminate containing the film layer of the present invention can be necked polypropylene spunbond, crimped polypropylene spunbond, bonded carded webs, elastomeric spunbond or meltblown fabrics produced from elastomeric resins. A particularly advantageous support layer is a fibrous nonwoven web. Such webs may be formed from a number of processes including, but not limited to, spunbonding, meltblowing and bonded carded web processes. Meltblown fibers are formed by extruding molten thermoplastic material through a plurality of fine, usually circular, capillaries as molten threads or filaments into a high velocity usually heated gas stream such as air, which attenuates the filaments of molten thermoplastic material to reduce their diameters. Thereafter, the meltblown fibers are carried by the high velocity usually heated gas stream and are deposited on a collecting surface to form a web of randomly dispersed meltblown fibers. The meltblown process is well-known and is described in various patents and publications, including NRL Report 4364, "Manufacture of Super-Fine Organic Fibers" by B. A. Wendt, E. L. Boone and D. D. Fluharty; NRL Report 5265, "An Improved Device For The Formation of Super-Fine Thermoplastic Fibers" by K. D. Lawrence, R. T. Lukas, J. A. Young; U.S. Patent No. 3,676,242, issued July 11, 1972, to Prentice; and U.S. Patent No. 3,849,241, issued November 19, 1974, to Buntin, et al. The foregoing references are incorporated herein by reference in their entirety.

Spunbond fibers are formed by extruding a molten thermoplastic material as filaments from a plurality of

- 14 -

fine, usually circular, capillaries in a spinnerette with the diameter of the extruded filaments then being rapidly reduced, for example, by non-educative or educative fluid-drawing or other well-known spunbonding mechanisms. The production of spunbond nonwoven webs is illustrated in patents such as Appel et al., U.S. Patent No. 4,340,563; Matsuki, et al., U.S. Patent No. 3,802,817; Dorschner et al., U.S. Patent No. 3,692,618; Kinney, U.S. Patent Nos. 3,338,992 and 3,341,394; Levy, U.S. Patent No. 3,276,944; Peterson, U.S. Patent No. 3,502,538; Hartman, U.S. Patent No. 3,502,763; Dobo et al., U.S. Patent No. 3,542,615; and Harmon, Canadian Patent No. 803,714. All of the foregoing references are incorporated herein by reference in their entirety.

A plurality of support layers 30 also may be used. Examples of such materials can include, for example, spunbond/meltblown laminates and spunbond/meltblown/spunbond laminates such as are taught in Brock et al., U.S. Patent No. 4,041,203 which is incorporated herein by reference in its entirety.

Bonded carded webs are made from staple fibers which are usually purchased in bales. The bales are placed in a picker which separates the fibers. Next the fibers are sent through a combing or carding unit which further breaks apart and aligns the staple fibers in the machine direction so as to form a machine direction-oriented fibrous nonwoven web. Once the web has been formed, it is then bonded by one or more of several bonding methods. One bonding method is powder bonding wherein a powdered adhesive is distributed throughout the web and then activated, usually by heating the web and adhesive with hot air. Another bonding method is pattern bonding wherein heated calender rolls or ultrasonic bonding equipment is used to bond the fibers together, usually in a localized bond pattern though the web can be bonded across its entire surface if so desired. When using

- 15 -

bicomponent staple fibers, through-air bonding equipment is, for many applications, especially advantageous.

The process shown in Figure 1 also may be used to create a three layer laminate. The only modification to the previously described process is to feed a supply 62 of a second fibrous nonwoven web support layer 30a into the laminating rolls 58 on a side of filled film 10 opposite that of the other fibrous nonwoven web support layer 30. As shown in Figure 1, one or both of the support layers may be formed directly in-line, as is support layer 30. Alternatively, the supply of one or both support layers may be in the form of a pre-formed roll 62, as is support layer 30a. In either event, the second support layer 30a is fed into the laminating rolls 58 and is laminated to filled film 10 in the same fashion as the first support layer 30.

As has been stated previously, filled film 10 and the breathable laminate 32 may be used in a wide variety of applications not the least of which includes personal care absorbent articles such as diapers, training pants, incontinence devices and feminine hygiene products such as sanitary napkins. An exemplary article 80, in this case a diaper, is shown in Figure 4 of the drawings. Referring to Figure 4, most such personal care absorbent articles 80 include a liquid permeable top sheet or liner 82, a back sheet or outercover 84 and an absorbent core 86 disposed between and contained by the top sheet 82 and back sheet 84. Articles 80 such as diapers may also include some type of fastening means 88 such as adhesive fastening tapes or mechanical hook and loop type fasteners to maintain the garment in place on the wearer, stretch region 90 in the waist area may also be provided for greater comfort

Filled film 10 by itself or in other forms such as the film/support layer laminate 32 may be used to form various portions of the article including, but not

- 16 -

limited to, stretch region 90, the top and the back sheet 84. If the film or laminate is to be used as the liner 82, it will most likely have to be apertured or otherwise made to be liquid permeable. When using a film/nonwoven laminate as the outercover 84, it is usually advantageous to place the nonwoven side facing out away from the user. In addition, in such embodiments it may be possible to utilize the nonwoven portion of the laminate as the loop portion of the hook and loop combination.

Other uses for the filled film and breathable film/support layer laminates according to the present invention include, but are not limited to, surgical drapes and gowns, wipers, barrier materials and articles of clothing or portions thereof including such items as workwear and lab coats.

The advantages and other characteristics of the present invention are best illustrated by the following examples:

EXAMPLES

For Examples 1 and 2 and comparative Examples 1 and 2, the best procedures described below were used to evaluate the films and laminate.

Cycle Test

A 3" wide by 6" long strip of the sample material was pulled to an elongated length of 160% and 200% of the original grip distance of 3 inches. The sample is elongated at a rate of 20 in/min for two cycles. Upon return after the second cycle, the elongation at which no load is first detected is recorded. This value is used as the final length in the immediate recovery calculation below.

- 17 -

$$(I) \quad \text{Immediate Recovery} = \frac{\text{Maximum Length} - \text{Final Length}}{\text{Maximum Length} - \text{Initial Length}} \times 100\%$$

5 The sample is then held at zero elongation for one minute. At this time, the sample is elongated until a load is detected. This value is used as the final length to calculate delayed recovery.

$$(II) \quad \text{Delayed Recovery} = \frac{\text{Maximum Length} - \text{Final Length}}{\text{Maximum Length} - \text{Initial Length}} \times 100\%$$

10 Hysteresis Loss

15 A 3 inch wide by 6 inch long strip of each sample is stretched to 160% of its unbiased length. The stretching apparatus was SINTECH Model 1/5 or Model 2/5 from Syntech Division of MTS Systems Corp., Research Triangle Park, NC 27709-4226. This cycle of 60% elongation was repeated two times. The % hysteresis loss was calculated in accordance to Equation III below.

$$(III) \text{ Hysteresis} = 100\% \left(\frac{\text{area under loading stress / strain curve} - \text{area under unloading stress / strain curve}}{\text{area under loading curve}} \right)$$

20 Tensile Test

 A 3" wide by 6" long strip of each sample was elongated at a rate of 20 in/min until it broke. Peak load and elongation at peak load were acquired.

25 Permanent Elongation

 An evaluation was performed to determine the amount of permanent elongation of the film and comparative materials.

30 A 3 inch wide by 6 inch long strip of each sample was stretched with the Syntech equipment described above. Each strip was stretched to 160% the unbiased length and held at the stretched length for one minute. The zero

- 18 -

load extension value, which is the distance that the jaws of the tensile test equipment move at the beginning of the second cycle before a load is registered by the equipment, was obtained from the tensile test equipment. The zero load extension value was then used to calculate %set with Equation V below.

$$(IV) \quad \% \text{ set} = \frac{\text{zero load extension after one cycle}}{\text{initial sample gauge length}} \times 100\%$$

After the second cycle, the sample was held at 60% elongation for one minute. The sample is then returned to zero elongation. Upon this return, the length at which no load is initially detected is used as the final length for the Immediate Set calculation below:

$$(V) \quad \text{Immediate Set} = \frac{\text{Final Length} - \text{Initial Length}}{\text{Final Length}}$$

The sample is then held at zero elongation for one minute. At that time the sample is elongated until a load is detected. The length at which this load is detected is used to calculate Delayed Set:

$$(VI) \quad \text{Delayed Set} = \frac{\text{Final Length} - \text{Initial Length}}{\text{Final Length}}$$

Recovery is defined as the difference between immediate set and delayed set. No recovery indicates that the two values were identical.

Water Vapor Transmission Data

The water vapor transmission rate (WVTR) for the sample materials was calculated in accordance with ASTM Standard E96-80. Circular samples measuring three inches in diameter were cut from each of the test materials and

- 19 -

a control which was a piece of CELGARD® 2500 film from Hoechst Celanese Corporation of Sommerville, New Jersey. CELGARD® 2500 film is a microporous polypropylene film. Three samples were prepared for each material. The test dish was a number 60-1 Vapometer pan distributed by Thwing-Albert Instrument Company of Philadelphia, Pennsylvania. One hundred milliliters of water were poured into each Vapometer pan and individual samples of the test materials and control material were placed across the open tops of the individual pans. Screw-on flanges were tightened to form a seal along the edges of the pan, leaving the associated test material or control material exposed to the ambient atmosphere over a 6.5 centimeter diameter circle having an exposed area of approximately 33.17 square centimeters. The pans were placed in a forced air oven at 100°F (32 °C) for 1 hour to equilibrate. The oven was a constant temperature oven with external air circulating through it to prevent water vapor accumulation inside. A suitable forced air oven is, for example, a Blue M Power-O-Matic 60 oven distributed by Blue M Electric Company of Blue Island, Illinois. Upon completion of the equilibration, the pans were removed from the oven, weighed and immediately returned to the oven. After 24 hours, the pans were removed from the oven and weighed again. The preliminary test water vapor transmission rate values were calculated with Equation (I) below:

$$(I) \text{ Test WVTR} = (\text{grams weight loss over 24 hours}) \times 315.5 \text{ g/m}^2 / 24\text{hrs}$$

The relative humidity within the oven was not specifically controlled.

Under predetermined set conditions of 100°F (32 °C) and ambient relative humidity, the WVTR for the CELGARD® 2500 control has been defined to be 5000 grams per square meter for 24 hours. Accordingly, the control sample was

- 20 -

run with each test and the preliminary test values were corrected to set conditions using equation II below:

$$(II) \quad WVTR = (\text{Test WVTR} / \text{control WVTR}) \times (5000 \text{ g/m}^2 / 24\text{hrs.})$$

5

EXAMPLE 1

A blown film of the composition (% by weight) listed in Table I below was extruded:

Table I

55% Supercoat™ calcium carbonate,
average particle size of 1 micron, available from English
China Clay Company of America, Sylacauga, AL,
45% Affinity™ 8200 resin (0.870 g/cc, 5 MI),
an (ethylene 1-octene) copolymer made with a single-site
catalyst, available from Dow Chemical Co. of Midland, MI, and
600± ppm of an antioxidant package.

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The 20-inch wide 1.5 mils thick film was then stretch-oriented in the machine direction (MD) at a stretch ratio of 5.4X (fast niproll speed divided by the slow nip speed), all rolls being at room temperature (65-70°F). Film inlet speed was 30 fpm, outlet speed 162 fpm on the MDO, and the stretched film was wound up at about 98 fpm so that the film could be wound up under the lowest tension. This gives an effective stretch ratio of 3.25X from film inlet to the MDO to the winder. The film was completely whitened indicating porosity, with a measured WVTR of 1618 g/m²/day. The film displayed very good elastic behavior in both the CD and MD direction.

- 21 -

The film so made was tested for its elastic behavior using tests which are described later following the examples. Testing the samples in the cross direction (CD), that is, perpendicular to the direction of orientation, average of four specimens tested, resulted in the values listed in Table II below.

Table II

Property	at 60% elongation	at 100% elongation
immediate recovery	71.31%	63.92%
immediate set	17.22%	36.08%
delayed recovery	85.27%	80.59%
delayed set	8.84%	19.41%
first cycle hysteresis loss	59.7%	67.9%
2 nd cycle hysteresis loss	39.0%	44.6%
peak (breaking) tensile load	334.0 grams	
peak (breaking) elongation	660.4%	

COMPARATIVE EXAMPLE 1

A commercially available breathable film, EXXAIRE™ XBF-511W, available from Exxon Chemical Company of Houston, TX, was also tested using some of the above test procedures. This film, essentially inelastic, has an undisclosed amount of filler, it is a uniaxially oriented microporous LLDPE film with WVTR of 3840 g/m²/day as measured by the test procedure described above. Cycle testing was done perpendicular to the direction of orientation. The values obtained are listed in Table III below:

Table III

Property	at 60% elongation
immediate recovery	39.9%
delayed recovery	73.5
first cycle hysteresis loss	86.7%
2 nd cycle hysteresis loss	67.9%
peak (breaking) tensile load	975 grams
peak (breaking) elongation	245%

COMPARATIVE EXAMPLE 2

A cast film of the following composition (% by weight) was extruded:

- 22 -

60% Supercoat™ calcium carbonate, as in Example 1

40% Exceed® 357C80, a metallocene-catalyzed
(ethylene 1-butene) copolymer (0.917 g/cc, 3.4 MI),
available from Exxon Chemical Co. of Houston, TX,
and

1000± ppm of an antioxidant package.

The extruded 1.5-mil thick film was then stretch-oriented in the machine direction at a stretch ratio of 4X, the preheat rolls, slow and fast niprolls set at 170°F and the annealing roll at 200°F. Film inlet speed was 100 fpm, and the stretched film was wound up at about 400 fpm. The film was completely whitened, and the measured WVTR was 4590 g/m²/day. This film was also tested perpendicular to the direction of orientation. The values obtained are listed in Table IV below.

Table IV

Property	at 60% elongation
immediate recovery	51.6%
delayed recovery	70.4%
first cycle hysteresis loss	79.25%
2 nd cycle hysteresis loss	57.4%
peak (breaking) tensile load	394.0 grams
peak (breaking) elongation	269%

Although this film is made with a metallocene-type of copolymer, it is essentially inelastic because of the higher density of the copolymer.

EXAMPLE 2

A blown film of the following composition (% by weight) was extruded:

55% Supercoat™ calcium carbonate, average particle size of 1 micron, available from English China Clay Company of America, Sylacauga, AL,

- 23 -

5 45% Affinity™ 8200 resin (0.870 g/cc, 5 MI), an
(ethylene 1-octene) copolymer made with a single-
site catalyst, available from Dow Chemical Co. of
Midland, MI, and

600± ppm of an antioxidant package.

10 The 20-inch wide 1.5 mils thick film was then
stretch-oriented in the machine direction (MD) on
equipment commonly known in the art as MDO, at a stretch
ratio of 5.0X (fast niproll speed divided by the slow
niproll speed), all rolls being at room temperature
15 (about 70°F), except the last roll which was set at 120°F
to anneal the film. Film inlet speed was 60 fpm, outlet
speed from the MDO was 300 fpm, and the film was then
directed to a winder whose speed was adjusted to allow
the film to relax but without any slack or sag before the
20 winder. A sheet of necked spunbond (previously stretched
to neck to 40% of its original width, ending basis weight
of 0.9 ounce per square yard) was then unwound, directed
under a spray-head, which was positioned between the MDO
and the winder, where the spunbond was sprayed with a
25 molten hotmelt (Rextac™ RT-2330, available from Rexene
Corp. of Odessa, TX) at adhesive add-on level of 3
grams/m², the so-sprayed spunbond was then directed to
niprolls just before the winder where the film and the
spunbond were contacted to consummate the lamination, and
30 the laminate was wound up at a speed of 155 fpm. The
laminate so made had a smooth, cloth-like appearance on
one side, it was soft and elastic (extensible with snap-
back) in the CD-direction withstanding repeated
stretching without delamination. The laminate was
35 breathable with WVTR measured at 1374 g/m²/day.

The laminate so made was tested for its elastic
behavior using tests described above. Testing the sample
in the cross direction (CD), that is, in the direction of

- 24 -

its extensibility and perpendicular to the direction of film orientation, average of four specimens tested, the values obtained are listed in Table V below:

Table V

Property	at 60% elongation	at 100% elongation
immediate recovery	70.73%	66.30%
immediate set	17.56%	33.50%
delayed recovery	85.64%	82.87%
first cycle hysteresis	68.2%	76.6%
2 nd cycle hysteresis	42.0%	48.2%
peak (breaking) tensile load	2,326.4 grams	
peak (breaking) elongation	221.7%	

Therefore, the films of the present invention have high water vapor transmission rate and elasticity that impart a wide variety of functionalities including vapor permeability, liquid impermeability, and comfort fit and stretch. Furthermore, such films can be attached to support layers to form laminates.

Of course, it should be understood that a wide range of changes and modifications can be made to the embodiments described above. It is therefore intended that the foregoing description illustrates rather than limits this invention, and that it is the following claims, including all equivalents, which define this invention.

- 25 -

CLAIMS:

1. A breathable laminate comprising:

an elastomeric film including a metallocene
catalyzed ethylene-based polymer having a density of from
about 0.850 to 0.899 g/cc and at least 30% by weight of a
filler having a particle size that contributes to pore
formation; and

at least one support layer bonded to said film
layer.

2. The laminate of claim 1 wherein said metallocene
catalyzed ethylene-based polymer is selected from
copolymers of ethylene and butylene, copolymers of
ethylene and hexene, copolymers of ethylene and octene
and combinations thereof.

3. The laminate of claim 1 wherein said film has an
unbiased length, a stretched length of about 160% said
unbiased length and an immediate recovery length;
said immediate recovery length is at least about 55%
said unbiased length following a stretch cycling that
achieved said stretched length.

4. The laminate of claim 1 wherein said film has an
unbiased length, a stretched length of about 200% said
unbiased length and an immediate recovery length;
said immediate recovery length is at least about 50%
said unbiased length following a stretch cycling that
achieved said stretched length.

5. The laminate of claim 1 wherein said density is from
about 0.860 to about 0.899 g/cc.

6. The laminate of claim 1 wherein said density is from
about 0.870 to about 0.899 g/cc.

- 26 -

7. The laminate of claim 1 wherein said filler is present in an amount of from about 40 to about 70% by weight of said film.

5

8. The laminate of claim 1 wherein said filler is present in an amount of from about 45 to about 60% by weight of said film.

10

9. The laminate of claim 1 wherein said filler is calcium carbonate.

10. The laminate of claim 1 wherein said filler particle size is from about 0.5 to about 8 microns.

15

11. The laminate of claim 1 wherein said film has a water vapor transmission rate of at least about 300 g/m²-24 hr.

20

12. The laminate of claim 1 wherein said film has a water vapor transmission rate of from about 1,000 to about 4,500 g/m²-/24 hr.

25

13. A personal care absorbent article comprising a liquid permeable top sheet and a back sheet with an absorbent core disposed therebetween, at least one of said back sheet or said top sheet including the laminate of claim 1.

30

14. The article of claim 13 further including at least one stretch region peripherally disposed on said article, at least one of said back sheet, said top sheet and said stretch region including the laminate of claim 1.

35

15. The article of claim 13 wherein said article is a diaper.

- 27 -

16. The article of claim 13 wherein said article is a training pant.

5 17. The article of claim 13 wherein said article is a sanitary napkin.

18. The article of claim 13 wherein said article is a incontinence device.

10

19. A process for preparing a breathable laminate comprising:

providing a polymeric resin including a metallocene catalyzed ethylene-based polymer having a density of from
15 about 0.850 to about 0.899 g/cc;

adding to said polymeric resin at least 30% by weight of a filler having a particle size that contributes to pore formation to form a filled resin;

20

casting a film from said filled resin, said film having a first length;

stretching said film to form a microporous film having a second length; and

bonding at least one support layer to said film to form a laminate.

25

20. The process of claim 19 wherein said ethylene-based polymer material is selected from copolymers of ethylene and butylene, copolymers of ethylene and hexene, copolymers of ethylene and octene and combinations
30 thereof.

21. The process of claim 19 wherein said density is from about 0.860 to about 0.899 g/cc.

35

22. The process of claim 19 wherein said density is from about 0.870 to about 0.899 g/cc.

- 28 -

23. The process of claim 19 wherein said film is stretched in a machine direction.

5 24. The process of claim 19 wherein said second length is from about 160% to about 450% said first length.

10 25. The process of claim 19 wherein said filler is present in an amount of from about 40 to about 70% by weight of said film.

15 26. The process of claim 19 wherein said filler is present in an amount of from about 45 to about 60% by weight of the film.

27. The process of claim 19 wherein said filler is calcium carbonate.

20 28. The process of claim 19 wherein said filler particle size is from about 0.5 to about 8 microns.

25 29. The process of claim 19 wherein said microporous film has a water vapor transmission rate of at least about $1000 \text{ g/m}^2\text{-24 hrs.}$

30 30. The process of claim 19 wherein said film has a water vapor transmission rate of from about 300 to about $4,500 \text{ g/m}^2\text{-24 hr.}$

31. A breathable laminate prepared by the process of claim 19.

35 32. A medical garment comprising a breathable laminate including a breathable elastomeric film and a support layer, said film comprising:

- 29 -

a metallocene catalyzed ethylene-based polymer
having a density of from about 0.850 to about 0.899 g/cc
at least 30% by weight of a filler having a particle
size that contributes to pore formation.

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33. The medical garment of claim 32 wherein the support
layer is bonded to one surface of said elastomeric film.

10

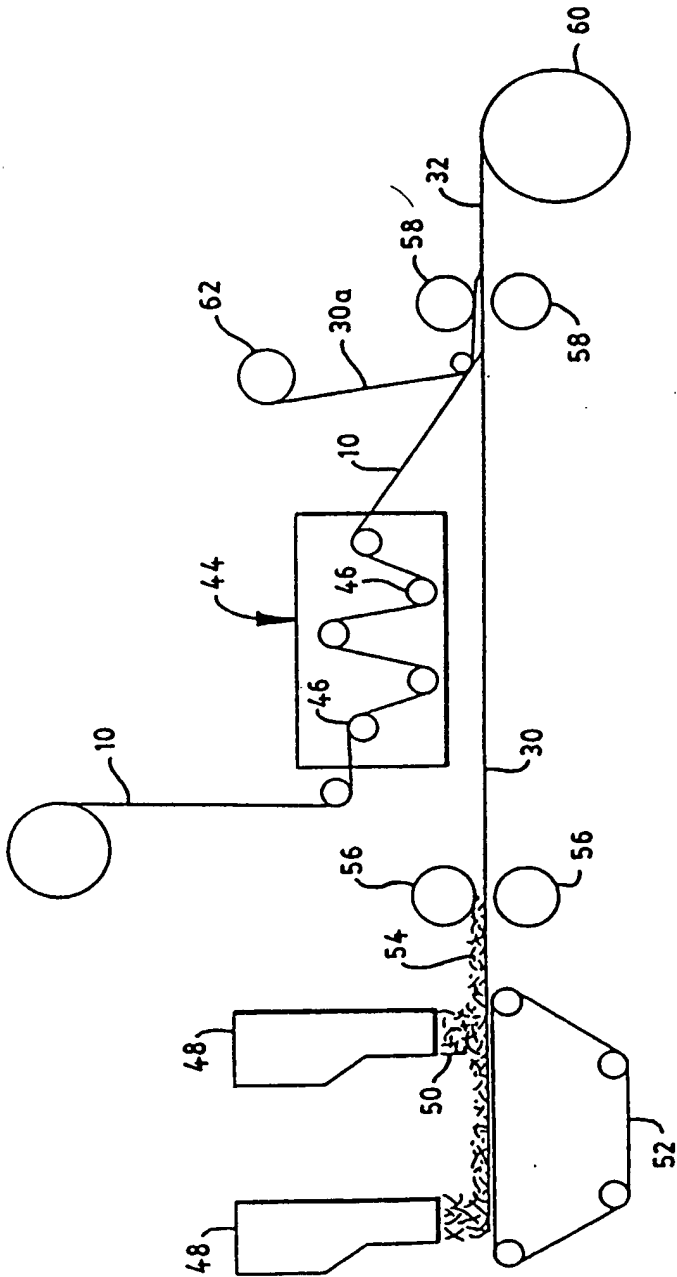


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/23264

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/12 C08J5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 605 831 A (MITSUBISHI PETROCHEMICAL CO) 13 July 1994 see abstract see page 2, line 5 - line 11 see page 2, line 52 - page 3, line 8 see page 4, line 11 - page 7, line 41 see page 9, line 42 - line 53 see page 10, line 53 - page 11, line 24 ---	1-33
Y	WO 95 16562 A (KIMBERLY CLARCK CORP) 22 June 1995 see page 3, line 17 - page 4, line 30; claims see page 10, line 3 - line 25 see page 13, line 11 - line 31 --- -/--	1-33

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Inte: onal Application No

PCT/US 97/23264

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 04955 A (BLESSINGS CORP) 13 February 1997 see page 11, line 1 - page 14, line 1; claims 1,12,30,31 see page 22, line 8 - line 12 ----	1-33
A	PATENT ABSTRACTS OF JAPAN vol. 095, no. 008, 29 September 1995 & JP 07 118431 A (MITSUBISHI CHEM CORP), 9 May 1995, see abstract ----	1-33
A	EP 0 659 808 A (TOKUYAMA CORP) 28 June 1995 see page 3, line 5 - line 32; claims ----	1-33
P, A	EP 0 779 325 A (MITSUI TOATSU CHEMICALS) 18 June 1997 see page 3, line 34 - line 43; claims ----	1-33
P, A	PATENT ABSTRACTS OF JAPAN vol. 097, no. 007, 31 July 1997 & JP 09 077893 A (MITSUI PETROCHEM IND LTD), 25 March 1997, see abstract -----	1-33

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/23264

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0605831 A	13-07-94	JP 6256594 A	13-09-94
		DE 69314616 D	20-11-97
		DE 69314616 T	05-03-98
		US 5385972 A	31-01-95
		JP 7026076 A	27-01-95
WO 9516562 A	22-06-95	AU 1335395 A	03-07-95
		BR 9408329 A	19-08-97
		CA 2116081 A	18-06-95
		CN 1142798 A	12-02-97
		EP 0734321 A	02-10-96
		FR 2713983 A	23-06-95
		FR 2717737 A	29-09-95
		GB 2285408 A, B	12-07-95
		JP 9506656 T	30-06-97
		PL 315183 A	14-10-96
		US 5695868 A	09-12-97
		ZA 9410026 A	22-08-95
WO 9704955 A	13-02-97	AU 6682896 A	26-02-97
EP 0659808 A	28-06-95	CN 1113179 A	13-12-95
		DE 69407149 D	15-01-98
		DE 69407149 T	26-03-98
		JP 7228719 A	29-08-95
		US 5445862 A	29-08-95
EP 0779325 A	18-06-97	JP 9221560 A	26-08-97